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DRAWINGS ATTACHED

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(19)



(54) PROCESS FOR THE PREPARATION OF ARYL-1,1,2,2-TETRAFLUOROETHYL ETHERS

(71) We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister Lucius & Brüning, a body corporate organised according to the laws of Germany, of 6230 Frankfurt (Main) 80, Postfach 80 03 20, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides a process for the preparation of an aryl-1,1,2,2-tetrafluoroethyl ether by reacting a phenolic compound, as hereinafter defined with tetrafluoroethylene in an organic solvent in the presence of an alkaline catalyst, which comprises contacting a solution of from 0.5 to 50% by weight of a phenolic compound in a water-miscible, polar solvent inert toward tetrafluoroethylene under the reaction conditions, preferably dimethylformamide, hexamethyl-phosphoric acid triamide or dimethylsulphoxide in the presence of from 0.05 to 0.5 mole of an alkali metal hydroxide per equivalent of phenol as hereinafter defined at atmospheric pressure or slightly reduced pressure and at a temperature of from 50 to 150°C with tetrafluoroethylene.

US Patent Specification No. 2,409,274 discloses the preparation of phenyl-1,1,2,2-tetrafluoroethyl ether by addition of tetrafluoroethylene to phenols. In the single example concerning phenol, the reaction is carried out in the course of about 12 hours at 100°C under pressure in an autoclave in the presence of metallic sodium as catalyst and benzene as solvent. The phenyl-1,1,2,2-tetrafluoroethyl ether is obtained with a yield of 4.6%.

D. C. England *et al* (J. Am. Chem. Soc. 82, 5116—2122 (1960)) have found an improvement to this process, using dimethylformamide or dioxan as solvents, the operation being carried out under pressure (2 to 2.7 atmospheres gauge) and at temperatures of from 60 to 100°C. Instead of metallic

sodium, W. A. Shephard (Journal of Organic Chemistry 29, 1—11 (1964)) employed in this process sodium hydride in dispersed form.

The reaction of sodium phenolate with tetrafluoroethylene in dimethylformamide under a relatively high pressure, the sodium phenolate being formed *in situ* from phenol and sodium, is described in US Patent No. 3,277,068.

Belgian Patent Specification No. 741 243 discloses that phenols may be reacted under pressure with tetrafluoroethylene in the presence of alkali metal hydroxides or alkali metal phenolates, if a certain amount of water is present and a certain critical molar ratio of tetrafluoroethylene to phenol is maintained. In the Belgian Patent Specification Nos. 691,603 and 691,604 there is also mentioned the reaction of nitro- or aminophenols with tetrafluoroethylene under pressure in the presence of alkali metal or alkaline earth metal hydroxides, sodium hydride or sodium methoxide as the catalyst and dimethylformamide or dioxan as the solvents.

All these processes have the disadvantage that the operation must be carried out under pressure, which necessitates expensive security measures due to the easily explosive decomposition of tetrafluoroethylene.

It has therefore been desirable to find a process which may be performed without the use of superatmospheric pressure and with a catalyst which is easy to handle and which renders superfluous the use of anhydrous solvents. Experiments of this type have hitherto been fruitless. Thus, J. W. C. Crawford (J. Chem. Soc. 1967, 2396) has stated that phenol in the presence of sodium phenolate, formed *in situ* from sodium metal and phenol, and dimethylsulphoxide or dimethylformamide does not react with tetrafluoroethylene at normal pressure.

It is therefore surprising that tetrafluoroethylene reacts easily with phenols at atmospheric pressure to form the corresponding

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aryl-tetrafluoroethyl ethers in good yields, if instead of the metallic sodium or sodium hydride, an alkali metal hydroxide is used as catalyst and if a water-miscible, polar solvent, preferably dimethylformamide, hexamethyl-phosphoric acid trisamide or dimethylsulphoxide is used. The reaction proceeds so easily that the reaction may be carried out even at a slightly reduced pressure.

As the phenolic starting compound there may be used for example, phenol itself or mono-, di- or tri-substituted phenol or a di- or polyhydric phenol, which may be unsubstituted or substituted provided that not more than four substituents, including the hydroxy groups, are present. As substituents that may be present in the phenyl nucleus there may be mentioned, more especially straight-chain or branched alkyl groups having preferably up to 20, especially up to 4 carbon atoms, alkoxy groups having up to 6, especially up to 4 carbon atoms, and formyl, amino, mono-alkylamino or dialkylamino group having preferably up to 4 carbon atoms in each alkyl moiety, as well as the piperidino and the morpholino group and alkanoylamino groups having up to 6 carbon atoms in the alkane moiety, especially acetamino groups. Furthermore, there may be used a polynuclear phenol for example, a naphthol which may be substituted or unsubstituted. The term "phenolic compound" is to be understood to include polyhydric phenols and polynuclear phenols. The solvent is not necessarily anhydrous and may be used without difficulty in a technical quality. The phenol is dissolved in this solvent in a concentration of from 5 to 50% by weight, advantageously from 10 to 30% by weight, preferably from 15 to 20% by weight. As the catalyst there is used an alkali metal hydroxide, preferably potassium hydroxide, advantageously in amounts of from 0.05 to 0.5, preferably from 0.15 to 0.3 mole, per equivalent of phenol, this being dissolved in the phenolic solution. One "equivalent of phenol" is a mole of phenol divided by the number of the phenolic hydroxy groups in the phenol molecule.

The reaction may be carried out by passing tetrafluoroethylene over the intensively stirred reaction mixture heated to about 50 to about 150°C, preferably to 70 to 130°C. The reaction proceeds more rapidly if the phenolic solution is passed over a heated packed column and the tetrafluoroethylene is introduced in to this column at normal pressure, where it is absorbed.

The reaction speed is different for the different phenols. In many cases the reaction is exothermic; it is completed when the absorption of tetrafluoroethylene is finished.

The reaction products are usually isolated by distillation of the obtained mixtures, the solvent being recovered or by treating the reaction mixture with water; the reaction product is precipitated and the solvent as well as the catalyst are transferred into the aqueous phase.

The reaction products are useful intermediates for the preparation of dyestuffs, pharmaceuticals and biocides.

The following Examples illustrate the invention.

Example 1

o-sec.-Butylphenol was reacted with tetrafluoroethylene in the device represented by the accompanying drawing. For this purpose, 75 g (0.5 mole) of *o*-sec.-butylphenol were dissolved in 240 g of dimethylformamide and 7 g (0.125 mole) of KOH were added. The whole was stirred until a solution was obtained, heating being optionally necessary. The flask (1) of the reaction device was filled with the resulting solution. The flask (1) and the column (2) were rinsed with nitrogen from the pressure vessel (3) and then with tetrafluoroethylene from the stock vessel (4) by means of the feed lines (5) and (6). Then the flask (1) (by means of the heating bath (7)) and the column (2) were heated to 90°C. The pump (8) was started, so that the solution trickled through the feed line (9) and through the column (2). The inner temperature regulated by the thermostat (10) amounted to 87°C. After starting the pump (8), the consumption of tetrafluoroethylene began immediately. The levelling vessel (11) was so adjusted that the pressure was not far below normal pressure. (12) is an outlet valve. As a result of the exothermic reaction, the temperature increased to 100°C. After 18 minutes, the absorption of tetrafluoroethylene was completed.

The reaction product was obtained with a 99% purity by precipitating with water, drying with sodium sulphate and subsequent fractionation. (115 g (92%) of 1 - tetrafluoroethoxy - 2 - sec. - butyl - benzene, boiling point $_{94}^{\circ}\text{C}$, n_D^{25} 1.4314).

The reaction products of other phenols with tetrafluoroethylene obtained in analogous way are listed in Table 1 as Examples 2 to 18.

TABLE I

Example No.	Product	charge			reaction temperature (°C)	reaction time (hours min.)	yield % of the theoretical	boiling point °C (mm)	melting point (°C)
		Phenol (mole)	catalyst (mole)	solvent (g)					
2	$OCF_2 \cdot CF_2H$ 	1.0	KOH (0.2)	DMF (250)	94-95	45 2.	75.2	86.5 85.	
3	"	0.5	KOH (0.125)	DMSO (240)	93-94	34 0.	73.3		
4	$OCF_2 \cdot CF_2H$ 	0.5	KOH (0.125)	DMF (240)	93-100	31 0.	99.5	112 12.	
5	$OCF_2 \cdot CF_2H$ 	0.5	KOH (0.25)	DMF (240)	86-93	00 1.	61.0	91-92.5 15.	
6	$OCF_2 \cdot CF_2H$ 	0.5	KOH (0.25)	DMF (240)	88-92	19 0.	75.0	106-103 11.	
7	$OCF_2 \cdot CF_2H$ 	0.5	KOH (0.125)	DMF (240)	87-100	18 0.	92.0	94 20.	

TABLE 1 continuation)

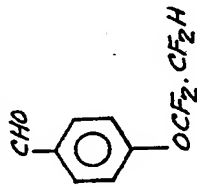
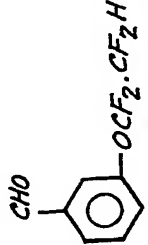
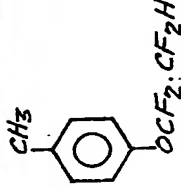
Example No.	Product	charge			reaction temperature (°C)	reaction time (min. hours)	yield % of the theoretical	boiling point (°C mm)	melting point (°C)
		phenol (mole)	catalyst (mole)	solvent (g)					
8		0.5	KOH (0.25)	DMF (240)	91-97	33 0.	67.0	100-102 12.	
9		0.5	KOH (0.25)	DMF (240)	94-98	00 1.	~49	103 13.	
10		0.5	KOH (0.125)	DMF (240)	46-57	57 0.	81	61 12.	

TABLE 1 (continuation)

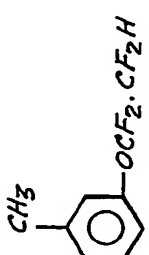
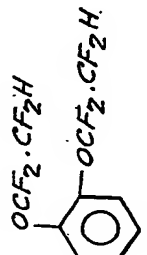
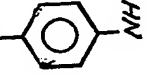
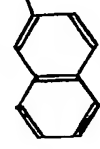
Example No.	Product	charge			reaction temperature (°C)	reaction time (min. hours)	yield % of the theoretical	boiling point (mm °C)	Melting point (°C)
		phenol (mole)	catalyst (mole)	solvent (g)					
11		0.5	KOH (0.125)	DMF (240)	85-96	26 0.	89.4	59 13.	
12	"	0.5	KOH (0.125)	DMSO (270)	86-100	31 0.	63.7		
13	"	0.5	KOH (0.125)	HPTA (255)	83-78	51 0.	83.7		
14	"	0.5	NaOH (0.125)	DMF (240)	93	51 0.	69.5		
15	"	0.5	K ₂ CO ₃ (0.125)	DMF (240)	90-91	27 1.	76.0		
16		0.5	KOH (0.25)	DMF (240)	88-90	41 2.	83.8	97-100 32.	

TABLE 1 (continuation)

Example No.	Product	charge			reaction temperature (°C)	reaction time (min. hours)	yield % of the theoretical	boiling point (mm °C)	melting point (°C)
		Phenol (mole)	catalyst (mole)	solvent (g)					
17	$OCF_2.CF_2H$ 	0.5	KOH (0.125)	DMF (240)	93-95	32 0.	99.6	—	117
18	$OCF_2.CF_2H$ 	0.5	KOH (0.125)	HPTA (255)	60-54	00 4.	68.6	—	29

DMF = Dimethylformamide

DMSO = Dimethylsulphoxide

HPTA = Hexamethyl-phosphoric acid trisamide

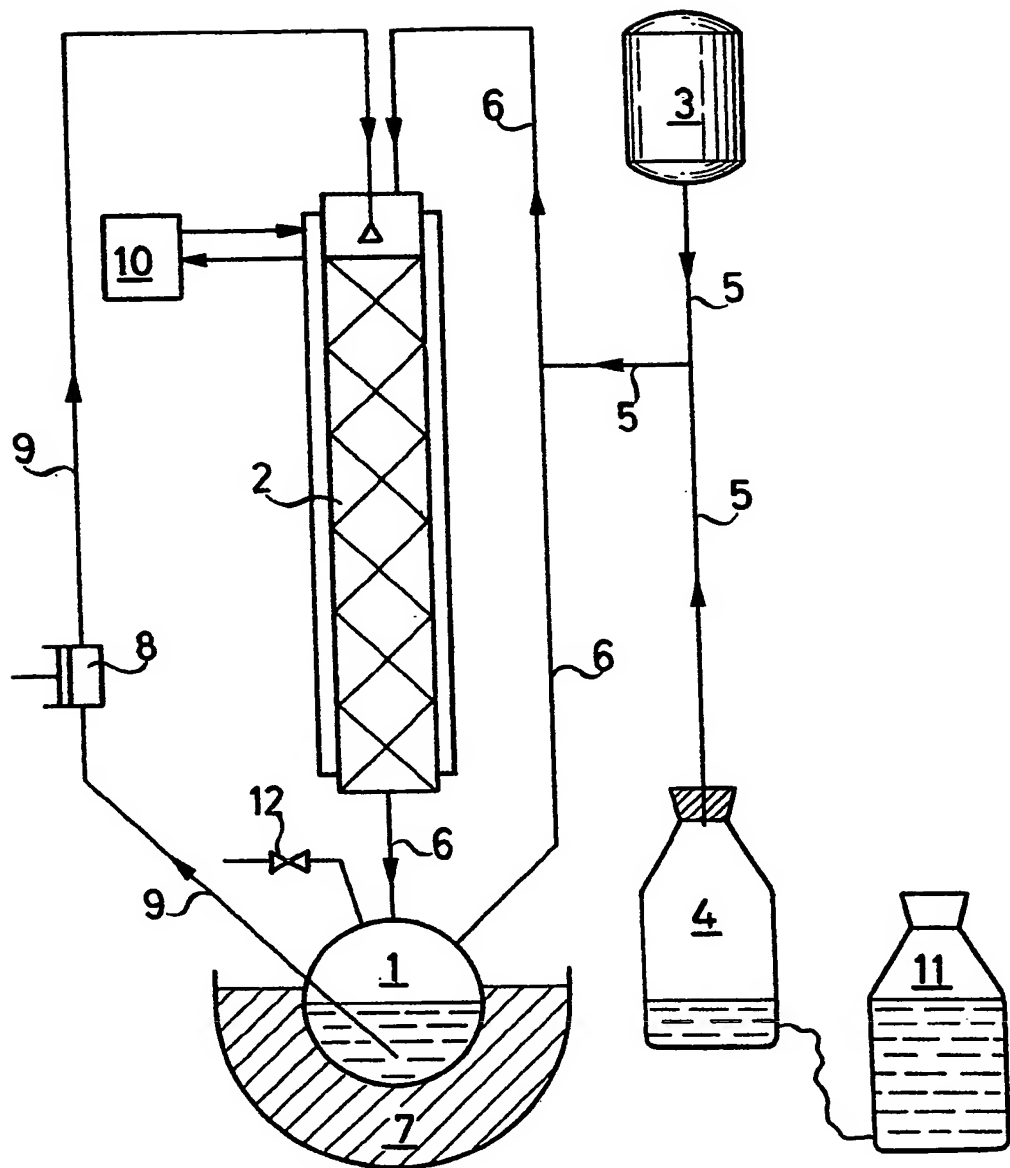
WHAT WE CLAIM IS:—

1. A process for the preparation of an aryl-1,1,2,2-tetrafluoroethyl ether, which comprises reacting a solution of from 5 to 50% by weight of a phenolic compound as hereinbefore defined in an inert polar water-miscible solvent with tetrafluoroethylene in the presence of from 0.05 to 0.5 mole of an alkali metal hydroxide per equivalent of phenol, as hereinbefore defined at a temperature of from 50 to 150°C and at atmospheric pressure or slightly sub-atmospheric pressure.
2. A process as claimed in claim 1, wherein the phenolic compound is phenol.
3. A process as claimed in claim 1, wherein the phenolic compound is phenol containing up to 3 substituents in addition to the hydroxy group.
4. A process as claimed in claim 1, wherein the phenolic compound is a di- or polyhydric phenol, which may be unsubstituted or substituted, provided that not more than four substituents, including the hydroxy groups, are present.
5. A process as claimed in 1, wherein the phenolic compound is a polynuclear phenol, which may be unsubstituted or may contain up to 3 substituents in addition to the hydroxy group.
6. A process as claimed in any one of claims 3 to 5, wherein the substituent is selected from alkyl groups having up to 20 carbon atoms, alkoxy groups having up to 6 carbon atoms, formyl, amino, monoalkylamino or dialkylamino groups having in each alkyl moiety up to 4 carbon atoms, piperidino and morpholino groups and alkanoylamino groups having up to 6 carbon atoms in the alkane moiety.
7. A process as claimed in claim 6, wherein the alkyl and alkoxy groups have up to 4 carbon atoms.
8. A process as claimed in any one of claims 1 to 7, wherein the solvent is dimethyl formamide.
9. A process as claimed in any one of claims 1 to 7, wherein the solvent is dimethyl sulphoxide.
10. A process as claimed in any one of claims 1 to 7, wherein the solvent is hexamethyl-phosphoric acid triamide.
11. A process as claimed in any one of claims 1 to 10, wherein the solution contains from 10 to 30% by weight of phenolic compound.
12. A process as claimed in any one of claims 1 to 11, wherein the solution contains from 15 to 20% by weight of phenolic compound.
13. A process as claimed in any one of claims 1 to 12, wherein the alkali metal hydroxide is used in an amount of from 0.15 to 0.3 mole per equivalent of phenol.
14. A process as claimed in any one of claims 1 to 13, wherein the alkali metal hydroxide is potassium hydroxide.
15. A process as claimed in any one of claims 1 to 14, wherein the reaction temperature is in the range of from 70 to 130°C.
16. A process conducted substantially as described in any one of Examples 1 to 18 herein with reference to and as shown in the accompanying drawing.
17. An aryl-1,1,2,2-tetrafluoroethyl ether whenever obtained by a process as claimed in any one of claims 1 to 16.

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